Solidification of Ultrasonically Levitated o-Terphenyl Crystals: A Raman Study.

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ABSTRACT

Ultrasonic levitation of millimeter size o-terphenyl crystals was carried out in a variable temperature enclosure. The trapped crystals were melted (m.p.= 331 K), undercooled and then seeded in order to initiate solidification. The incidence of an Argon laser beam served as a non-contact probe during the containerless processing. Elastic scattering and low frequency (< 200 cm⁻1) shifted inelastic Raman scattering resulting from lattice vibrational modes were simultaneously monitored. The Raman spectra undergo remarkable changes during phase transformation, as well as, track inter-molecular structural reconfiguration occurring in the solid and liquid states. Raman scattered light by virtue of its incoherence dots not suffer from interference effects associated with coherence encountered in elastic scattering, and there.fore proved to be a reliable tool for monitoring the kinetics of phase transformation during containerless processing of transparent materials. Thus the continuously monitored peak intensity of the most prominent Raman lattice feature was used to measure the volume fraction transformed as a function of time during solidification at different untie.rcooling levels. Growth rates during crystallization of o-terphenyl were inferred from this information. The extent to which these growth rates fit an existing solidification model was tested.

1. INTRODUCTION

Ultrasonic levitation [1] has served as a means for containerless processing (CP), namely, melting and undercooling [2.,3] of millimeter-size, low melting point materials. A primary motivation for containerless processing has been the elimination of heterogeneous nucleation induced by contact between the melt and container walls. This in turn enables the attainment of larger undercooling levels, thereby creating the opportunity, in some cases, for metastable and/or amorphous structures to be achieved, Ultrasonic levitation provides a means for CP of glasses, ceramics and organic materials, in the laboratory, as well as, in the microgravity environment of space. The latter approach being favored where larger quiescent melts are desired. other potential applications utilizing ultrasonic levitation based CP could be the study of homogeneous nucleation and ice formation from single undercooled water drops, in a cent rolled environment [4].

While ultrasonic levitation along with other containerless techniques [5] eliminate contact between container wall and sample, the availability of suitable non-contact diagnostics is crucial to extracting the desired scientific information. For instance, the ability to monitor sample temperature, chemistry, inter-molecular structure., and the rates of transformation during phase change, *in-situ*, can prove extremely beneficial towards promoting a better understanding of solidification.

Spectroscopic diagnostics based on laser interrogation, followed by monitoring of inelastic light (Raman scattering and fluorescence emission) is a proven diagnostic for a wide variety of processes involving levitated samples. '1'0 name just a few, Raman spectroscopy of electrodynamically levitated micrometer size. particles has been used to monitor chemistry [6,7] and fluorescence thermometry [8] enabled an evaporation study of a single acoustically levitated water drop. Recently the use of Raman spectroscopy as a means for monitoring CP of an acoustically levitated crystal of *o*-terphenyl (0"1'1') was reported [10]. in this report, Raman spectral features identified in a previous study using bulk samples [11] were found to serve as viable indicators of inter-molecular structural changes accompanying phase transformations during CP.

The present work, extends the study of Raman diagnostics as a tool for monitoring melting, undercooling and solidification of levitated transparent *o*-terphenyl samples. Lattice vibrational Raman spectra [12] sensitive to inter-molecular structural changes during

CP have been utilized. Levitated samples of OTP were subjected to stepped as well as continuous temperature changes. Stepped temperature changes followed by isothermal holding allowed spectral scanning over the region of interest, while continuous heating and cooling was tracked by monitoring the peak intensity of the strongest Raman lattice feature. Raman spectral profiles qualitatively demonstrate. the inter-molecular structural changes occurring during CP. The continuously tracked Raman peak intensity, on the other hand, has been used to determine the volume fraction transformation rates during solidification.

The fact that remarkable changes in Raman spectral features associated with lattice vibrations occur during the transformation from crystalline solid to liquid has long been recognized [13]. For crystals, incident photons of wave vector q Raman-scatter (Stokes) inelastically with a wave vector q' such that:

$$\hbar q - \hbar q' = \hbar k$$

(1)

where $\hbar$ is Planck's constant divided by 2π and k is the wave vector associated with the lattice phonon modes. Fundamental one-phonon optical transitions result from these interactions, where $k=0$, for crystals (see ref. 12 for further details). On melting or transforming to an amorphous or disordered state the $k=0$ selection rule breaks down, however, allowing contributions from all the vibrational modes of the material toward the overall inelastic scattering. The intensity associated with each mode being weighted by an optical coupling tensor [14,15]. Thus the summation over the modes can be replaced by the density of vibrational states function, which is the number of modes per unit frequency interval. This function governs the thermodynamic properties of the disordered state.

The discussion above implies that in the crystalline state well defined lattice peaks observable in the Raman spectra, degenerate to a broad band upon transformation to the disordered (liquid or glassy) state. The well defined crystalline, peak locations and widths arc determined by temperature and its influence on the lattice (thermal expansion) as well as internal stresses. The broader spectra associated with the disordered state, on the other hand, arc related to the vibrational density of states function. This has been utilized, for instance, to determine the temperature dependence of heat capacity in vitreous silica [16] and tile specific heat of ice [17]. The disordered state Raman spectra has also been used to determine the size of micro-cry ystallites in glass ceramics [18]. A microscopic theory with possible applications to some model systems for the disordered state spectra has also been reported recentl y [19]. Thus tracking of Raman spectra through phase changes and

subsequent undercooling has the potential of yielding valuable lattice or inter-molecular structural information. While other techniques based on x-ray and neutron diffraction yield similar information, the relative case of performing Raman spectroscopy *in-situ* should be recognized.

A fundamental difference, between elastic and inelastic or Raman scattering from an assembly of molecules, based on purely classical considerations [20] is as follows. The elastic interaction preserves phase information rendering the scattered light from different molecules coherent and therefore can undergo interference with itself as well as incident unscattered light. Such interference effects are particularly complicated for solids and liquids. Raman scattering is an incoherent process and does not preserve phase information, This ensure.s that the scattering observed from an assembly of individual scattering centers is always additive. Consider for example, a two phase sample. comprised of solid crystalline and liquid phases, as encountered during melting or solidification. The crystal exhibits a strong lattice vibrational mode, which is absent or severely suppressed in the liquid. The argument is made that the Raman intensity of the lattice line measured over a given solid angle from such a sample, is indicative of the relative volume fraction of the two phases whereas the. elastic scattering over an identical solid angle may not give a true representation of the respective volume fractions because of complications arising due to interference.

2. EXPERIMENTAL

A schematic top-view of the experimental layout is depicted in Figure 1, Details of the acoustic levitator and enclosure are described elsewhere [1,3]. Quartz windows around the enclosure allow entry of the interrogating Argon ion laser beam (wavelength, $\lambda = 514.5$ nm) as well as collection of video, elastic and inelastic (Raman) signals from the levitated sample. The interrogating laser beam is expanded and then focused using lens 1. which is positioned such that the beam spot radius incident on the sample is -2. times larger than the equivalent sample radius. in this manner 100-200" mW of laser power is brought to incidence on the levitated sample..

Raman lattice vibrational lines for organic materials usually display Raman shifts less than 200 cm^{-1} from the interrogating laser frequency, consequentl y, a holographic notch filter (1 INF) is used with the collection lens assembl y (1.1 & 1.2) shown in Fig. 1. This arrangement allows discrimination against the strong laser background before the scattered

light enters the double grating (1 200 lines/mm) monochromator. The use of the HNF allows reliable Raman shift measurements starting at -50 cm^{-1} from the interrogating laser frequency. This was verified by reproducing the Raman spectral profiles excited at laser wavelengths of 488 and 514,5 nm, respectivel y, together with the appropriate HNF's. During the present work it was established that the light transmission function of the I INF is extremely sensitive to the angular orientation of the filter with respect to the collected light. Thus the appropriate transmission for the orientation used (14.S degrees) in our measurements, was determined independently with the aid of a tungsten lamp.

As shown in Figure 1, the laser light rejected by the HNF can be measured by photodiode 2, thus the arrangement allows elastic and Raman light collected over an identical solid angle, to be simultaneous] y monitored. An additional detector (Photodiode 1) monitors the forward scattered laser light at thirty degrees. Photodiode 1 and 2 signals, recorded continuously during sample processing, allow not only a comparison between Raman and elastic scattering, but serve as a passive record of the levitated sample positional stability. Slit widths of 50 and 100 micrometers have been used during this work. A cooled (243 K) GaAs photomultiplier tube (PM"]') serves as the detector for the Raman scattering and its output is fed through a preamplifier to a photon counter.

Video records of the sample during processing are made. A typical video sequence observed during processing has been reported elsewhere [11].

Millimeter size (equivalent sample diameter -1.2 mm) irregular shaped solid crystals of 0'1'1' arc deployed in the acoustic trap. Levitated samples exhibit good positional stability at fixed temperatures. Fluctuations of the order of -50 micrometers or less, in the center of mass position occur. These fluctuations arc usually lateral rather than vertical. The trapped crystals occasionally exhibit rotation at 3 to 10 Hz about a fixed center of mass. The incident laser spot being larger than the sample allows satisfactory signal collection under these circumstances. During thermal cycling, the sound velocity in the ccl] medium (air in the present case) changes. This has to be compensated by adjusting the separation between the acoustic driver and reflector, in order to maintain a standing acoustic wave, While heating, the center of mass of solid crystals tends to drop vertically downwards. Once molten, the samples assume an oblate spheroidal shape with aspect ratios ranging between 1.10-1.16, the larger values being for larger samples, The liquid drops obtained upon melting undergo some amount of rotation about the axysymmetric axis (1-7 revolutions pcr

second), as well as, exhibit complex internal flows. These inevitably arise because of the high ultrasonic fields required for levitation in the presence of a gravitational field. Molten samples are held at or slightly above the. melting point for a few minutes and then undercooled to the desired extent, During subsequent undercooling of molten samples, they tend to flatten i.e. assume higher aspect ratios, as well as the center of mass tenets to move upward. in the present set of experiments heating and cooling rates employed are such that sample positional and shape (only for molten samples) drifts are compensated manually by adjusting the. acoustic driver and reflector separation by means of a micrometer translator.

Once undercooled, solidification is induced by "seeding". Seeding consists of dropping a few fine] y crushed grains of crystal powder on the molten sample with the help of a syringe while avoiding contact between the melt and syringe tip.

Cell temperature is recorded by an embedded thermocouple (TC in Figure 1) positioned in the proximity of the levitated sample (-1 cm). The thermocouple reading is believed to be within 1-4 K of true sample temperature. The deviation arises due to two reasons. Firstly, acoustic streaming [21] associated with the high sound pressure levels (SPL) required for levitation (140- 165 dB) results in a the.rmal lag between the sample temperature and thermocouple reading, because based on their respective locations in the cell the extent of forced convection varies. Secondly, laser heating affects the sample true temperature which the thermocouple dots not faithfully sense. For the size of samples used in the present study melting was observed to occur within 0.5 K of the meltingpc)intof01'1](331 K), in the absence of the laser beam. With laser light incident cm the sample melting occurred within 1-4 K below the melting point. The variation observed from sample to sample is believed to be caused by unknown amounts of impurity and the effect they have on altering the optical absorption. The crystals used for processing were obtained from a melt Of 99% pure OTP supplied by Aldrich Chemical Co. Once the crystals arc trapped, however, air borne dust particles cannot be prevented from contacting the sample surface since a scaled enclosure. for levitation was not used .

3. RESULTS

Figure 1 a displays typical spectra acquired during different processing stages of a levitated OTP sample. The accompanying legend shows the cell temperature during the acquisition

of each spectrum, namely, following sample deployment at mom temperature (296 K), after heating upto and holding at 318 K, and finally after melting and allowing the cell temperature 10 stabilize at 331 K for - 10 minutes. A spectral bandpass of $\sim 3 \, cm^{-1}$ was used to acquire these spectra. The solid state crystalline spectra exhibit a profile consisting of peaks, nominally around 123 and 146 cm^{-1} with a minor but discernible feature spanning the region from $\sim 75\text{-}86 \, cm^{-1}$. As the cell is heated from room temperature to ~ 318 K all the peaks exhibit a shift to lower frequencies. Based on many such observations, not shown, the peak frequencies arc found to decrease linearly with increasing temperature. This behavior is attributed to thermal expansion causing a weakening in the intermolecular bonding [12]. The liquid spectrum after melting, on the other hand, reveals nearly a complete absence of all the previously noted spectral features characterizing the crystalline state, leaving a broad band. This observation is consistent with a breakdown of the selection rules mentioned earlier.

The spectra displayed in Figure 1 a dots not take into account the light transmission of the 1 INF. Figure 1 b shows the corrected and smoothed spectra. All the peaks shift to lower frequencies by $\sim 3 \, cm^{-1}$. "This was not recognized in previous investigations [10,11] where the appropriate transmission function for the 11 NF was not used. New reproducible spectral features also emerge after applying the correction. These arc, the peaks at -67 and 82 cm^{-1} and shoulders at ~ 87 and 108 cm^{-1}. The liquid spectra revealed after the correction shows a weak remnant of all the previously noted solid lattice peaks but they are nearly merged with the background again because the contributions from all the phonon modes are now comparable. However, the spectra do suggest that some partial ordering or remnant lattice dots persist in the liquid state,.

The solid state spectra of Fig 1 b displays six reproducible features including the shoulders. OTP crystallizes in a monoclinic structure and like p-terphenyl [22] ant] naphthalene [20,2.3] is expected to posses two molecules per unit cell and therefore should exhibit at least six Raman active vibrational mode.s, Of course additional peaks shifted less than 50 cm^{-1} which cannot be reliably ascertained because of the attenuation of the IINF cannot be ruled out. in organic crystals in addition to phonon features ring-ring modes and low lying torsion's are, not uncommon. It would be reasonable to assume, however, that at least some of the features shown in Figure 1 arc due to Raman active librational modes.

Figure 2a shows spectra acquired from a different sample than the one discussed above. 1 lere spectral changes displayed by the liquid after melting arc shown. These were

obtained with a spectral bandpass of $6\,cm^{-1}$. The first spectrum at 331 K represents the liquid immediately after melting. The next spectrum was acquired after holding the liquid drop above melting point for ~10 minutes, during which time the cell temperature increased to 333 K. Finally a spectrum was acquired following undercooking below the melting point to 318 K and then allowing the ccl] temperature to stabilize. Qualitative differences in intensity and line shape are apparent. The spectral intensities shown in Fig 1 a when corrected for the HNF transmission and reduced by the normalized Bose-Einstein population factor, $(1+n(\omega))/\omega$, following the explanation given in reference [15] appear as shown in Figure 2b, where:

$$n(\omega) = [\; \exp(\frac{\hbar\omega}{kT}) - 1]^{-1} \qquad (2)$$

ω being the angular frequency of scattering, k the Boltzmann constant and T the absolute temperature. These reduced intensity distributions are related to the vibrational density of states function in the liquid. The different intensities depicted in Figure 2 do not arise due to shape changes of the liquid ()'1'1' drop. This was verified by acquiring spectra from suspended drops of OTP and here too similar intensity changes could be confirmed. Thus in Figure 2b the spectrum obtained immediatel y following melting seems broad with poorl y resolved spectral features. However, after holding above the melting point the overall intensity drops but the spectra] features which were also observed in Figure 1 b emerge. Upon undercooling the spectrum resembles the appearance noted immediately following melting with some alterations in profile. The significance of these observed changes is not properly understood. Even though efforts were made to equilibrate cell temperature, changes in the spectr a Occurring during acquisition cannot be ruled out. Thus the results shown in Figure 2b merely suggest that not only do remnants of the Raman active vibrational modes appear in the liquid state but they also undergo changes with temperature and time of residence. The significance of these changes in determining the "liquid structure" and its influence if any on solidification characteristics deserves further study under more controlled conditions of sample purity, polarization discrimination of scattering and faster spectra] acquisition times.

Limitations in the present experimental capability have necessitated interrupting the processing, such as, stepped heating followed by isothermal holds, in order to obtain the Raman spectral profile. However, experiments in which the peak Raman (123 cm 1) intensity is monitored in real time during processing have been performed. In previous

reports [10,11] such measurements were shown to serve. as indicators of melting, glass transition and re-solidification, since large discontinuous changes in the monitored intensity accompanied these transformations. in the present study melting, re-solidification and undercooling of levitated samples were studied by simultaneously monitoring the Raman peak and elastic scattering intensity collected at ninety degrees and thirty degrees. The simultaneously monitored elastic signals serve as an aid to confirming gross shape or positional fluctuations in the sample during processing. A meaningful comparison between elastic and Raman can only be made by comparing the signals collected over an identical solid angle as is the case with the ninety degree elastic scattering. All references to elastic scattering made henceforth refer to this ninety degree scattered signal. Furthermore the advantage of tracking the Raman intensities over the elastic for process monitoring is also demonstrated by the results, as discussed below.

Figure 3 shows a typical data set obtained while monitoring the melting of a levitated o-terphenyl crystal, where: (a) the Raman peak intensity (b) the elastic scattering and (c) the cel] temperature record are shown. in the processing run depicted by Figure 3 the sample was deployed in the pre-heated and equilibrated cell at 320 K, The rate of change of both the Raman peak and the elastic intensity show two distinct regimes, the first slower varying region lasting from -300 to 450 seconds, followed by a more abrupt decrease. After correlating these signals with the video record the following interpretation was arrived at. Melting originates on the surface of the crystal where droplets form initially and subsequently coalesce to form a film on the crystal surface. This film of melt continues to grow until the volume fraction of liquid is substantial enough for the remaining solid to be engulfed in a drop of the melt. This entire process is represented by the slower rate of change of signal. Once enough liquid forms to engulf the residual solid, the latter is stirred around in the newly formed drop due to the. inevitable levitation related internal flows and is quickly transformed into liquid. This second stage after drop formation is represented by the rapid change in Raman and elastic signal levels. While the relative duration of the processes mentioned vary from sample to sample they can be identified in all the samples processed.

The temperature record indicates that the cc11 temperature changes from -327 to 330 K during the melting. Since the melting point of o-terphenyl is 331 K the lower observed temperature for initiation of solidification is attributed to laser heating as well as the uncertain role played by unknown amounts of impurity.

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Several other noteworthy and reproducible feature.s are revealed in Figure 3. The elastic signal displays a lot of fluctuation which is not seen in Raman intensity. This is attributed to the interference effects in the elastic scattering which arc further aggravated by sample rotation and internal flows, The Raman peak intensity seem less sensitive to these artifacts and therefore serves as a better tool for diagnostic and monitoring purposes.

The Raman intensity is always seen to increase just prior to the onset of melting while the elastic scattering remains relatively flat. Furthermore, the exact time at which the Raman and elastic scattering start decreasing do not coincide exactly and neither do their rates of change. A suitable explanation for these observations is not available at present.

Figure 4 shows data acquired while processing of the same sample as in Figure 3 but at a later stage, during undercooling. Here while the Raman peak intensity undergoes a steady rise between -2800 and 3200 seconds the elastic signal maintains a relatively steady baseline Both the signals display fluctuations, however, and a correlation of these. fluctuations with the video record indicates that most of this arises due to shape fluctuation in the liquid drop. 1 lowever, instances of sample center of mass fluctuations arc also apparent in the region spanning 2950-3000 seconds. Even though the acoustic levitator is being continuously manually adjusted to preserve the drop shape and position aspect ratio fluctuations cannot be completely suppressed. The increase in the Raman intensity observed in the data shown in Figure 4 is similar to the spectral intensity increase displayed in Fig 2..

Finally solidification initiated by seeding at different undercooking levels was studied. Figure 5a displays a compilation of the change in the Raman peak intensity from three different sample processing runs. The cell temperature was equilibrated prior to seeding and is indicated in the accompanying legend. Figure 5b shows the simultaneously recorded elastic intensity where large fluctuations of intensity arising due to interference c. ffects obscure the transformation rate information. A comparison of Figure 5a and 5b underscores the argument made for the advantage of using incoherent Raman light for monitoring kinetics of transformation during phase change.

The S-shaped appearance of the Raman intensity variation represents the volume transformation rate of the liquid drop into a solid crystal, This shape is explained with the aid of a simple model which assume.s isothermal growth at a constant rote, starting from a seed initially located at the south pole of the spherical drop, The seeding powder upon

making contact with the drop gets entrained in the internal flow and tends to settle in the vicinity of the south pole of the drop, due to gravity effects. Growth proceeds from this polar location and proceeds at a uniform rate so that a spherical growth front centered at the south pole propagates till the entire drop is transformed into solid. The solid curves in Figure 5 were calculated assuming this simple model for the volume transformation rate. The equivalent radius of the actual sample and an appropriate constant growth rate R (shown in the legend) were used to fit the curves to the data. The equivalent radius was obtained from calibrated video images as well as verified gravimetrically using the crystals after solidification.

The mode.1 used is an idealization because stirring, of the initial solid fraction inevitably occurs. Moreover, growth may proceed from more than one location though eventually they merge into one growth front . The real shape of the solidifying sample in our case is an oblate spheroid with aspect ratio ranging from 1,10-1.16 but the simple model chosen ignores this fact. The deviation from the fit observed especially in the early stages of transformation in the data of Figure 5a is attributed to these artifacts. However, the overall degree of fit observed makes the inference of a constant growth rate at each undercooling level seem reasonable.

The heat of fusion for o-terphenyl, ΔH_f -4.40 kcal/mole [2.4] yields an entropy of fusion $\Delta H_f / T_m \sim 13$ which exceeds 4R, (Tm is the melting point and R is the universal gas constant, 1.98 cal/mole K). This suggests that o-terphenyl crystals possess a flat liquid-solid interface requiring a lateral growth mechanism [25]. Furthermore o-terphenyl is an organic material with branched molecules exhibiting a non-linear $\ln(\eta)$ vs $1/T$ behavior [24], η being the shear viscosity and T the absolute temperature. These criteria, and the assumption that growth occurs by a surface nucleation mechanism would validate the following representation of the growth rate [26]:

$$R = R_0 \exp(-C/(T-T_r)) \exp(-BT_m/T\Delta T) \qquad (3)$$

where R is the growth rate, R_0, C and B are constants, "T_r is a reference temperature, 'J' is the solidification temperature ant] ΔT is the undercooling. This relation is arrived at based on the. assumption that initially the growth rate will increase with undercooling, as will the viscosity of the melt. Eventually, however, the viscosity increase will dominate the overall process and slow down mass transport of molecules (o the growth interface, thus slowing down the growth rate.. The range of temperatures that could be explored in the present

experiment extended from T_m (331 K) to room temperature, since the levitator could not be further cooled using the current arrangement. over this temperature range the growth rates measured showed an increase. In order to attempt a first order fit with Eqn. 3 the following approximate procedure was followed. The term $\exp(-C/T-T_r)$ is supposed to account for the viscosity change and values of C and T_r which fit viscosity data for O'J'l' over a wide temperature range, overlapping the present, has been reported [24]. Using these values $C = 689$ K and "$J_r = 231$) $[\ln R + C/(T-T_r)]$ was plotted versus $1/T\Delta T$ and this plot yielded values for B and R_0. To a first order of approximation Eqn. 3 could be rewritten as:

$$R = -497\exp[-689/(T-231)]\exp(-15320/T\Delta T)\text{cm/sec}. \qquad (4)$$

Figure 6 shows the model obtained along with the measured data points. Obviously more data points arc needed to verify and refine. this growth model and this is left for a future study. From the value of B obtained above, and taking $B = (4as^2)/\Delta H_f k$ [26] where a is (hc lattice spacing of the growing crystallographic habit, s is the surface energy of the crystal and k is Boltzmann constant. Assuming a to be of the order 6-8 angstroms, s ranges from 3.4 to 4.3 erg/cm^2. "l'bough this value cannot be verified for OTP it compares favorably with the surface energy of other organic crystals such as 1,3,5-Tri-Napthylbenzene.

4. CONCLUSIONS

The Raman lattice spectra or inter-molecular vibrational spectra of OTP has been measured during thermal processing of a levitated millimeter size sample. Spectral changes representing inter-molec~j]ar structural changes in both the solid crystalline, and molten liquid forms have been identified and can serve as rate monitoring signals for phase transformations. The coherent elastic scattering cannot provide the. same amount of information as the incoherent Raman scattering.

Ample scope for improvement and refinement of the work reported exists. The main areas arc brie.f]y indicated. Sample. purity as attainable by developing a scaled and controlled environment cell would strengthen the validity of the findings. Raman monitoring using a state of the art multichannel detector, such as a charge coupled c] c(ccl or (CCD) or a photodiode array (PDA) will allow real time, simultaneous spectral and peak intensity measurements removing uncertainties encountered during the present work where scanning

was resorted to. A feedback control based on a position sensing diode signal driving a piezoelectric translator for maintaining sample position and shape would vastly improve positional stability and render the performance of such experiments much less laborious.

Since Raman signals are usually weak the photon counting time required to build up satisfactory signal to noise is the main limitation of this technique in terms of its applicability for *in-situ* studies. For example, dendritic growth which proceeds much faster than the faceted growth exhibited by *o*-terphenyl. However, the use of high repetition rate pulsed lasers may in some instances still render the technique viable. An extension of this approach to monitoring of processes such as oriented fiber pulling or single crystal growth of transparent materials cannot be overlooked.

ACKNOWLEDGMENTS

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Figure 1 (a) Raman lattice spectra during different stages of containerless processing of an acoustical] y levitated *o*-terphenyl crystal measured through a HNF with monochromator slits set at 3 cm"]. (b) The same. spectra after correction for the transmission function of the HNF and smoothing, spectral peaks and shoulders severely attenuated in Fig 1 a arc now revealed at 67, 82, 87 and 108 cm 1,

Figure 2 (a) Raman signal from the lattice spectra] region for molten liquid drops of o-terphenyl immediately after melting, after holding 2 K above melting point for 10 minutes and after undercooling to 318 K. (b) after correction for the HNF transmission and reduction by the normalized Bose-llinstcin population factor $\omega[1-t\ n(\omega)]^{-1}$. Qualitative changes in the spectral profiles and intensity indicative of structural rearrangement of the molecules arc apparent.

Figure 3 (a) Variation in the Raman lattice peak (-123 cm 1) intensity just prior to and during melting of *o*-terphenyl crystal; (b) elastic scattering variation simultaneously monitored with the Raman and (c) levitation ccl] temperature record.

Figure 4 Variation in simultaneously recorded (a) inelastic Raman peak intensity (b) elastic scattering and (c) cell temperature during the undercooling of a levitated molten drop of *o*-terphenyl.

Figure 5 (a) Raman peak intensity at 123 cm^{-1} variation from the initiation to completion of solidification for levitated *o*-terphenyl samples subjected to varying amounts of undercooling. The solid lines arc calculated volume transformation rates assuming solidification to proceed at a constant growth rate, R. (b) Simultaneously recorded elastic intensity during solidification where drastic intensity fluctuations arising from interference effects arc seen. These erratic intensity fluctuations render the elastic signal inappropriate for rate monitoring during solidification.

Figure 6 The solid line shows the growth model given by the relation (4) of text. The points arc the inferred growth rates obtained from the variation in the Raman peak intensity.

(a)

Raman Peak ntensity cps)

6000
5000
4000
3000
2000
1000
0

2400 2600 2800 3000 3?00 3400 3600

Time (secs.)

(b)

Elatic Intensity (mV)

1600
1400
12'00
1000
800
600
400
200
0

2400 2'600 ?800 3000 32oo 3400 36oo

Time (sees.)

(c)

Temperature (K)

328
326
324
3??
320
318

2400 ?600 2800 3000 3200 3400 3600

Time (sees.)

21

(a)

Raman Intensity (cps)

- ■ $\Delta T = 26 +/- 0.25$ K
- — R = 65 um/sec
- A $\Delta T = 14 +/- 0.25$ κ
- ---- R = 32 um/sec
- ● $\Delta T = 9 +/- 0.25$ K
- ······ R = 12 um/sec

Time (sees.)

(b)

Elastic ntensi y (mV)

- ■ $\epsilon \Delta T = 26 +/- 0.25$ K
- A e $\Delta T = 14 +/- 0.25$ K
- ● el $\Delta T = 9 -I/- 0.25$ K

Time (sees)